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Contact Adhesive

Addition to patent ..... (patent application P 23 29 035.9)

The main patent .....(patent application P 23 29 035.9) concerns the use of mixtures of ethylene copolymers and a natural or synthetic resin as a contact adhesive wherein one proceeds from a mixture:

- a) 80 to 30 wt.% of an ethylene copolymer that contains 25 to 50 wt.% of polymerized methyl acrylate and has a melt index that lies between 10 and 100 g/10 min. and
- b) 20 to 70 wt.% of a tackifying resin.

The invention proceeded from the assumption that mixtures comprising ethylene-ethyl acrylate-copolymers and/or an ethyl-butyl-acrylate-copolymers and a tacky additive are known and used in practice for the production of hotmelt adhesives. At room temperature these mixtures have a non-adhesive or weakly adhesive surface and therefore cannot be used as contact adhesives. Another disadvantage of these mixtures is the insufficient compatibility with tacky resins.

Therefore one task underlying the invention was to present contact adhesives with high heat resistance and cohesion, whose components are very compatible with each other and that do not become segregated during longer heat treatments.

In accordance with the invention it was found that this task can be solved by using a mixture of 80 to 30 wt.% of an ethylene copolymer that contains 25 to 50 wt.% of

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polymerized methyl acrylate and has a melt index that lies between 10 and 100 g/10 min. and 20 to 70 wt.% of a tacky resin.

It was then found that also a mixture in which the ethylene-methyl acrylate-copolymer has a higher melt index could be used successfully.

Thus the object of the present invention is the use of a modified ethylene-methyl acrylate-copolymers as the mixture component for contact adhesives wherein one proceeds from a mixture comprising:

- a) 80 to 30 wt.% of an ethylene copolymer that contains 25 to 50 wt.% of polymerized methyl acrylate and has a melt index that lies between 101 and 550 g/10 min. and
- b) 20 to 70 wt.% of a tacky resin.

The copolymers comprising ethylene and methyl acrylate to be used for the contact adhesives within the scope of the invention are produced by copolymerizing ethylene with methyl acrylate using pressures above 500 atm and temperatures between 150 and 400°C in the presence of radical polymerization initiators. Suitable ethylene-methyl acrylate-copolymers in accordance with the present invention contain 25 to 50 wt.% of polymerized methyl acrylate and have a melt index of 101 to 550 g/10 min. (measured at a temperature of 190°C and a weight of 2.16 kg in accordance with ASTM D 1238/65 T).

The said ethylene-methyl acrylate-copolymer is mixed with sticky additives, so-called tackifiers. Suitable tackifying resins are natural resins, modified natural resins and also synthetic resins. Tackifying resins are solid, amorphous, hard to brittle thermoplastic substances that soften at temperatures between 40 and 140°C and whose molecular weight and/or average molecular weight lies in general between 200 and 7 000.

Suitable natural resins and modified natural resins are, for example, terpene resins (also called polyterpene resins), balsam resins, rosins, colophony, hydrogenated colophony, ester of colophony or of hydrogenated colophony, for example, glycerol ester, pentaerythritol ester, ethylene glycol ester, diethylene glycol ester, triethylene glycol ester, propyl ester or methyl ester of the colophony and/or hydrogenated colophony. The hydroabietyl alcohol that arises during the complete hydrogenation of the colophony can also be used in the esterified form. For example, benzoic acid or phthalic acid is a suitable acid component. Good tackifying resins are also the common terpene resins and alkylphenol resins, also synthetic resins such as ketone resins, hydrocarbon resins such as for example, coumarone resins, indene resins or hydrocarbon resins derived from crude oil, styrene copolymers that are obtained by the polymerization of vinyl toluene and styrene or isobutylene and styrene. Also polyisobutylene that has a molecular weight of 1 000 to 50 000 (determined as per viscosity) is suitable for use as a tackifier.

It is preferred to use those resins that contain the least possible acid groups and whose acid value lies below 100, preferably between 0 and 20. It is also advantageous to use mixtures of different tackifying resins, for example, mixtures comprising two to four different resins. As long as mixtures of resins are used that have a varying softening point, for example, a mixture comprising resins with softening point at 70°C and resins with a softening point at 120°C, the derived contact adhesives can be used in a wider temperature range than using a contact adhesive that contains only one resin.

The mixtures are produced in conventional plants, for example, in a kneader, extruder or an agitator pan. The components can also be mixed in the presence of a solvent. Aromatic or chlorinated hydrocarbons are suitable for use as solvents. These include benzene, toluene, xylene, chlorobenzene, methylene chloride and chloroform. The mixtures can contain the additives that are usually added to ethylene copolymers, for example,

stabilizers, aging inhibitors, dyestuffs, pigments and waxes.

The mixture comprising ethylene-methyl acrylate-copolymers and a tackifying substance is applied on substrates, for instance by extrusion or rollers or with the help of casting machines. In addition, if the mixture is applied using a smelter, it is necessary to heat the mixture to temperatures between approximately 120 and 250°C. the mixture can also be applied on a substrate in the form of a solution at room temperature. However in that case, the solvent must be removed.

Examples of suitable substrates for the described contact adhesive compounds include paper, textile cloth comprising synthetic or natural fibers, non-woven fabrics, wood, rubber, metal, glass, bitumen surfaces, bituminized paperboards and plastic plates and/or plastic films. The contact adhesive compounds are applied, for example, on paper or sheets of polyethylene, polypropylene, polyvinyl chloride, polyethylene glycol terephthalate or polystyrene. In order to apply the contact adhesive compounds on heat sensitive foils, the so-called transfer process is used. This process involves the application of the adhesive compounds first as a film on release paper. After this film has cooled down, it is transferred on to the foil. The melt viscosity of the adhesive material without solvent amounts to 500 to 50 000 m · Pa · s at a temperature of 180°C.

The described adhesives are suitable for the production of self-adhesive compounds, for instance, self-adhesive films, self-adhesive labels, self-adhesive floor coverings, self-adhesive wall coverings, medical plasters and self-adhesive anti-drumming (sound absorbent materials).

The invention is elaborated in more detail on the basis of the following examples.

In the examples, 40 µm thick foils of polyethylene glycol terephthalate are coated with a 25 µm (equivalent to 25 g/m<sup>2</sup>) thick adhesive film. The adhesive can be applied as a

melted mass or as a solution (e.g. in toluene) on the polyethylene glycol terephthalate foil. If a solvent is used, it is necessary to dry off the solvent using reduced pressure. The temperature of the coated foil should not increase beyond approximately 130°C. For assessing the adhesive properties of the foil that is coated with the contact adhesive, the surface tack is determined using the probe tack test and the peel test after the drying process at room temperature and also after the 7-days of storage at a temperature of 70°C. In addition, the cohesion of the adhesive layer is determined using the peel test.

For examining the surface tack in accordance with the probe tack test and the peel test, a foil that is coated with the contact adhesive is cut into a 2 cm wide test strips that are stored for 24 hours before and after the heat storage at 70°C in a climatized room at a temperature of 20°C and a relative air moisture of 65%.

The probe tack test is carried out on a Polyken probe tack tester as has been specified in the Special Technical Publication No. 360 of the ASTM [American Society for Testing and Materials] (1963). The test is performed under the following conditions:

Contact time 0.2 sec., haul-off speed 2 cm/sec., weight 20 g/cm<sup>2</sup>.

In the peel test, the 2 cm wide test strips are stuck on a chrome plate and peeled parallel to the adhesive layer, i.e. in an angle of 180° and the force required for that is measured. The haul-off speed amounts to 300 mm/min. The measurement is taken 24 hours after the adhesion.

The shear test is performed in accordance with the method described in the DT-OS 2 134 688. The test strips are stuck on a high-gloss chrome-plated steel sheet with a surface area of 20 x 25 mm. The coated steel sheet is fixed vertically. The end of the adhesive strip is

loaded with 1 000 g and the time taken for the adhesion to peel away under the constant tensile force is calculated. The measurement is taken at 20 and 50°C.

#### Example 1

A 40  $\mu\text{m}$  thick foil of polyethylene glycol terephthalate is coated with a 25  $\mu\text{m}$  thick layer of a mixture of 50 parts of an ethylene methyl acrylate copolymer and 50 parts of a hydrogenated colophony, whose softening point lies in the range of 75 and 80°C. The ethylene copolymer contains 65 wt.% of ethylene and 35wt.% of methyl acrylate. It has a melt index of 150 g/10 min. The adhesive properties of the derived contact adhesive foil are compiled in the table below.

#### Example 2

Example 1 is repeated, however with the exception that an ethylene methyl acrylate copolymer is used that contains 60 wt.% of ethylene and 40 wt.% of polymerized methyl acrylate. The melt index of this polymer amounts to 150 g/10 min. The adhesive properties of the contact adhesive foil are stated in the table below.

#### Example 3

50 parts of the ethylene copolymer specified in example 1 are mixed with 50 parts of the phthalic acid of the hydroabietyl alcohol, whose softening point lies between 60 and 70°C. The mixture works as a contact adhesive and is applied on the foil specified in example 1 in strength of 25  $\mu\text{m}$ . A self-adhesive foil is derived whose properties are stated in the table below.

Example 4

50 parts of an ethylene methyl acrylate copolymer that contains 37 wt.% of methyl acrylate and having a melt index of 425 g/10 min. are mixed with 50 parts of a colophony resin that has been esterified with glycerol and that has a softening point that lies at 85°C. The properties of the contact adhesive foil are stated in the table below.

Example 5

60 parts of the ethylene copolymer described in example 4 are mixed with 40 parts of a terpene phenol resin at a temperature of approximately 190°C. The softening point of the terpene phenol resin lies in the range of 63 and 70°C. As specified in example 1, the mixture is applied on a foil of polyethylene glycol terephthalate in strength of 25  $\mu\text{m}$ . A self-adhesive foil is derived whose properties are stated in the table below.

Example 6

50 parts of the ethylene methyl acrylate described in example 4 are mixed at a temperature of approximately 190°C with 50 parts of an isobutylene/styrene resin that has a softening point of approximately 50°C. The foil specified in example 1 is coated with the mixture produced in this manner. The thickness of the coating amounts to 25  $\mu\text{m}$ . The properties of the derived contact adhesive foil are stated in the table below.

Example 7

70 parts of an ethylene methyl acrylate copolymer that contains 32 wt.% of methyl acrylate and having a melt index of 425 g/10 min. are mixed with 30 parts of a

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pentaerythritol ester or colophony. The softening point of the resin lies between 102 and 110°C. The contact adhesive foil produced in accordance with example 1 exhibits the adhesive properties that have been stated in the table below.

#### Example 8

80 parts of a copolymer in accordance with example 7 are mixed with 20 parts of a colophony that has been esterified with glycerol and whose softening point lies at 85°C. The table below shows the adhesive properties of the contact adhesive foil.

Table

Example no.	1	2	3	4	5	6	7	8
Peel strength								
after 24 hours	1 130	750	1 200	1 400	1 020	710	1 580 <sup>1)</sup>	980
after 7 days at 70°C	1 240	830	1 200	1 430	1 070	730	1 600 <sup>1)</sup>	1 000
Probe tack								
immediate	850	650	830	950	450	500	900	600
after 7 days at 70°C	620	470	740	900	430	490	950	620
Shear strength								
at 20°C								
after 24 hours	>3 days	>3 days	>3 days	>3 days	>3 days	>3 days	44 hours	>3 days
after 7 days at 70°C	>3 days	>3 days	>3 days	>3 days	>3 days	>3 days	50 hours	>3 days
Shear strength								
at 50°C								
after 24 hours	45'	55'	37'	36'	25'	28'	15'	16'
after 7 days at 70°C	60'	65'	45'	38'	30'	30'	18'	17'

<sup>1)</sup> Cohesion fracture

Patent claim

Use of a mixture comprising

- a) 80 to 30 wt.% of an ethylene copolymer that contains 25 to 50 wt.% of polymerized methyl acrylate and has a melt index that lies between 101 and 550 g/10 min. and
- b) 20 to 70 wt.% of a tackifying resin

as a compact adhesive.

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[initials]